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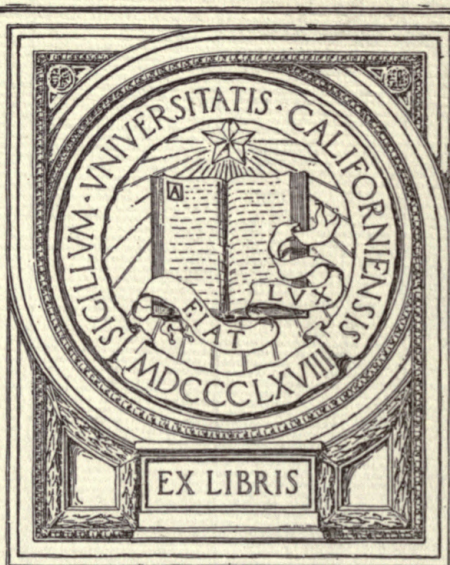
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The Formation of Addition Compounds Between Formic
Acid and Metallic Formates. A Discussion of
the Factors Affecting the Stability of
These Compounds.

by
HOWARD ADLER, B.S., M.A.

DISSERTATION



Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in
the Faculty of Pure Science of
Columbia University.

NEW YORK CITY
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The effect of addition of various foreign
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ACKNOWLEDGMENT

The author wishes to express to Professor James Kendall his sincere gratitude for the suggestion of the problem, and for his helpful advice throughout the course of the investigation.

The author also wishes to acknowledge with thanks the co-operation of the other members of the Chemistry Department of Columbia University.

ABSTRACT OF DISSERTATION

1. What was attempted?
2. In how far were the attempts successful?
3. What contribution actually new to the science of chemistry has been made?

1. The attempt was made to demonstrate the applicability of rules previously formulated governing the variation of addition compound formation, to systems of the type $HX \cdot RX$. The particular systems studied were the formic acid—metallic formate series. A few cases of the series acetic acid—metallic acetate were also studied.

2. (a) It has been shown that the extent of combination between formic acid and the metallic formates varies uniformly with the position of the metal (R) in the electromotive series. As the position of R changes from potassium through the series, the extent of compound formation decreases to a minimum (in the neighborhood of hydrogen). A similar variation occurs in the acetate systems, with a slight increase in the extent of combination when the position of R is considerably below hydrogen.

(b) It has also been shown that the variation in the extent of compound formation is parallel to the change in conductivity.

(c) The change in solubility follows regularly the change in compound formation.

3. (a) The initial steps in the formulation of a generalized theory of ionization have received additional experimental confirmation.

(b) Further development of methods for determining the existence and extent of compound formation in solution has been indicated.

(c) Evidence has been obtained of causal relationships between compound formation, conductivity, solubility, and diversity of components in systems of the general type $HX \cdot RX$.

(d) In the course of the investigation, five new acid formates have been isolated.

THE FORMATION OF ADDITION COMPOUNDS BETWEEN FORMIC ACID AND METALLIC FORMATES. A DISCUSSION OF THE FACTORS AFFECTING THE STABILITY OF THESE COMPOUNDS.

INTRODUCTION

In the preceding articles of this series¹, it has been conclusively demonstrated that the extent of compound formation in a solution depends essentially upon the difference in character of the two components. On the basis of the generalization² that compounds increase in stability uniformly with increasing divergence in the basic or acidic nature of the two components, it has been possible to predict the relative extents of combination in various systems, as well as the relative stability of the complexes formed. Agreement of experimental results with these predictions has been extremely satisfactory³.

The study of aqueous systems of the type $HX \cdot HOH$, and to a less extent, of the type $ROH \cdot HOH$ ⁴, revealed the fact that the generalization developed for non-aqueous solvents could be applied, with equally good results, to solutions in water. Practically complete predetermination of the extent of the reaction $HX + HOH \rightleftharpoons HX \cdot HOH$ from left to right was possible.

The results of the investigation mentioned above led to the correlation of ionization and compound formation⁵. It was shown that for systems of the type $HX \cdot HOH$, and $ROH \cdot HOH$, the extent of ionization varied directly with the extent of combination between the two components of the system. The causal relationship between the two phenomena, which this variation suggested, has been verified by Gross⁶. The conduc-

¹ Kendall and Booge, J. A. C. S. 38, 1712 (1916). For résumé see Kendall, Booge and Andrews, *ibid.*, 39, 2304 (1917).

² Lewis, System of Physical Chemistry, V. I, pg. 417.

³ The exceptional behavior of phenols has been noted. See Kendall, Booge and Andrews *loc. cit.* p. 2306; also Kendall J. A. C. S. 38, 1317, 1322 (1916); 36, 1240 (1914).

⁴ Kendall, Booge and Andrews, *loc. cit.*

⁵ Kendall and Booge, J. A. C. S. 39, 2323 (1917).

⁶ Gross, Columbia University Dissertation, 1919.

tivity measurements made by this investigator confirm the hypothesis that ionization in solution is preceded by compound formation between solvent and solute.

The generalization concerning compound formation was postulated for aqueous systems of the type $\text{ROH} \cdot \text{HOH}$ in the following form¹:

(a) No indication of hydrate formation with extremely weak bases.

(b) A regular increase in the extent of combination in the liquid state as the strength of the base is increased.

(c) Extensive compound formation with transition and strong bases.

(d) Increase in complexity² as well as stability of hydrates with the strength of the base.

Experimental verification of these statements for solutions of the type water-base (as afforded by the work of previous investigators) was presented at the time of their proposal. It is to an extension of this topic that the present paper is devoted. Additional data upon this problem are essential to a more general formulation of the ionic theory, since, as has already been mentioned³, more complete knowledge of the comparatively simple systems $\text{RX} \cdot \text{HX}$ and $\text{ROH} \cdot \text{RX}$ is necessary before any quantitative knowledge of the complex system $\text{RX} \cdot \text{H}_2\text{O}$ can be gained.

Solvent-Base-Systems. With a generalization of the theory of solutions will come, of necessity, a broadening of definitions, so as to remove the restrictions now imposed by the limited range of applicability of the accepted theory. In terms of the broader conceptions, a base is defined as a binary compound, which on solution yields the same negative ion as the negative radical of the solvent⁴. With this in mind, it is

¹ Kendall, Booge and Andrews, loc. cit. p. 2320.

² i. e. compounds of the type $(\text{ROH})_a(\text{HOH})_b$ can be isolated when there is considerable divergence between the components.

³ Kendall, Booge and Andrews, loc. cit., p. 2322.

⁴ This terminology has been used by Schlesinger and Calvert, J. A. C. S. 33, 1933 (1911).

obvious that the non-aqueous system $\text{HX} \cdot \text{RX}$ is identical in nature with the system $\text{ROH} \cdot \text{HOH}$. Hence it is of interest to see whether the postulates proposed for the latter type will hold equally well for the former. This condition is essential to the evolution of a more comprehensive theory of solutions.

Criterion of Diversity. Since diversity of the two components is postulated as necessary for combination between them, it becomes necessary to arrive at some criterion of the extent of divergence in systems of the type $\text{HX} \cdot \text{RX}$. The X radical being common to both components, the "difference" between H and R must afford a measure of the tendency to complex formation, i. e. of the tendency of the reaction $\text{HX} + \text{RX} \rightleftharpoons \text{HX} \cdot \text{RX}$ to go forward. The best available criterion of this divergence is the relative positions of the metal (R) and hydrogen in the electromotive series. This follows from the relationship which exists between the electromotive series (or electrode potential series, since these are identical in order) and the chemical activity of the metals¹. The relative activities of the metals are given by the order of the electromotive series, the activity decreasing in order from K down the series to the noble metals.

It is to be expected, then, that the higher the position of the metal (R) in the series, the stronger will be the resulting base (RX)². As R is varied, and approaches hydrogen, the strength of the resulting base, as evidenced by the extent of compound formation and, consequently³, of ionization, should diminish. In the immediate neighborhood of hydrogen, the base should be very weak. On continuing the variation beyond hydrogen, the difference between the components becomes more pronounced, the lower the position of the metal in the series. This divergence should result in the formation of

¹ For a full discussion of chemical affinity and its measurement by e. m. f., see particularly Lewis, *System Physical Chemistry*, V. 2, Ch. XII. Also Leffeldt, *Electrochem.*, pp. 181, 182, 194. Mellor, *Modern Inorganic Chem.*, 361-376; LeBlanc, *Electrochem.*, 267 et seq.

² This ought to be equally true, irrespective of the nature of X—i.e., whether it be NO_3 , SO_4 , OH —etc.

³ Kendall and Booge, loc. cit., p. 2324.

bases stronger than those of the metals located near hydrogen in the series¹.

It is seen that on the basis of the above assumption the strength of the base RX should diminish to a minimum and then increase again, as R is varied from one extreme of the electromotive series to the other. Those properties which are usually associated with the term "strength"—extent of ionization (compound formation), and, as will be seen from the sequel, solubility, should undergo concomitant variation. The experimental work to be described, will seek to establish the validity of this argument.

SYSTEMS $HX \cdot RX$. ACID SALTS.

There are in the literature numerous references to compounds of the type $(RX)_a(HX)_b$, i. e., acid salts. There have been, however, very few systematic investigations of such salts, with a view to the correlation of the fact of their existence with theory.

It might be worth considering briefly those compounds mentioned in the literature, in order to see how far they are in agreement with the requirement of the theoretical basis developed above. A complete survey would not be of any value, because such acid salts as bisulfites, bicarbonates, and others, could never lend themselves to systematic study, since the acids exist only in solution. The following review will be limited to those cases where the compounds can be obtained from the pure acid and base.

¹ The position of the metals in the electromotive series (or rather, electro-affinity) as a factor in determining the properties of metallic compounds, such as the chlorides, has been used by Bodlander, *Z. Phys. Chem.* 27, 55 (1898), and Abegg and Bodlander, *Z. Anorg. Chem.* 20, 453 (1899). They attempted to show for example, that the solubility of the chlorides increased as the position of the metal varied from bottom to top of the series, i. e. from Ag to K . This is notoriously not the case; which fact led to the use of additional hypotheses to maintain the original thesis. The procedure was not altogether warranted. The failure to establish the validity of the propositions advanced is probably due to the total neglect of the influence of the solvent. Furthermore, the systems examined were of the complex type $RY \cdot HX$ or $RY \cdot H_2O$, and the complications introduced by the fourth radical prevented any real connection between the electromotive series and properties such as solubility from being discovered.

The only acid whose acid salts have been completely examined is sulfuric acid¹. The results of the entire investigation are to be published shortly, so that a complete discussion of this system is not now advisable. The results in general are, however, in highly satisfactory agreement with the theory. There has been no other complete series studied, with any theoretical objective. The compounds mentioned in the literature, as conditioned above, are given in Table I, which follows:

TABLE I.

Solvent	Base	Compounds
HNO ₃	KNO ₃	KNO ₃ ·2HNO ₃ ² ; KNO ₃ ·HNO ₃ ²
	NH ₄ NO ₃	NH ₄ NO ₃ ·2HNO ₃ ² ; NH ₄ NO ₃ ·HNO ₃ ²
HAc	KAc	KAc·2HAc ³ ; KAc·HAc ⁴
	NaAc	NaAc·2HAc; NaAc·HAc ⁵
	NH ₄ Ac	NH ₄ Ac·HAc ⁶
	LiAc	LiAc·HAc ⁷
	TlAc	TlAc·HAc ⁷
HF	KF	KF·3HF ⁸ ; KF·HF ⁹
	NaF	NaF·HF ¹⁰
	LiF	LiF·HF ¹¹
	NH ₄ F	NH ₄ F·HF ¹²
	AgF	AgF·3HF ¹³ ; AgF·HF ¹³

The existence of all of these compounds, as well as that of the hydrates of bases which have already been enumerated¹⁴, is in agreement with the requirements of the theory. All

¹ Landon, J. A. C. S., 42, 2131 (1920). Completed by Davidson, as yet unpublished.

² Groschuff, Ber. 37, 1488 (1904). The same author's work on formic acid will be referred to in the following section.

³ Lescoeur, Ann. Chim. Phys. (6), 28, 245 (1893).

⁴ Melsens, Compt. Rend. 19, 611 (1844).

⁵ Lescoeur, loc. cit., pg. 241.

⁶ Reik, Monatshefte f. Chemie, 23, 1033 (1902).

⁷ Lescoeur, Bull. Soc. Chim., 24, 517 (1875).

⁸ Moissan, Compt. Rend., 106, 547 (1888).

⁹ Abegg, Hand. Anorg. Chem., 2-1, 343.

¹⁰ Abegg, ibid., 220-221.

¹¹ Ibid., pg. 120.

¹² Marignac, Ann. Min. (5) 15, 221 (1859).

¹³ Guntz, Bull. Soc. Chim. (3) 13, 114 (1895).

¹⁴ Kendall, Booge and Andrews, loc. cit., p. 2320.

metals whose "bases" form addition compounds of the acid-salt type, are either strongly electropositive or strongly electronegative. It is especially noteworthy that silver fluoride is soluble in hydrofluoric acid, and is extensively solvated.

It is evident that the data existing are not sufficient to supply a rigorous test of the validity of the argument. The varying reliability of results from scattered sources, the lack of completeness in all the series examined, as well as the absence of investigations of freezing-points so as to permit the determination of relative extents of combination throughout the series, all tend to diminish the value of any conclusion which may be drawn. For these reasons, it was deemed necessary to determine as completely as possible the freezing-point curves for the series formate-formic acid. In this series the only part which was varied was that which corresponds to R in the type system $RX-HX$. After the effect of this variation of R has been determined, the role of X can be more exactly examined, by a study of several series similar to the one in question.

FORMIC ACID AS SOLVENT

It has already been determined by Schlesinger and collaborators¹, that solutions of the formates in formic acid are excellent conductors. The alkali formates are highly ionized, and are entirely analogous to the alkali hydroxides in water. It has also been shown² that the conductivity of a solution depends upon two factors—(a) the extent of compound formation and (b) the extent of dissociation of the complexes into ions of opposite charge. Since the metallic formates form highly conducting solutions in formic acid, it follows that they are highly solvated in solution.

The formates in formic acid should give rise to compound formation, varying in extent with the position of the metal in the electromotive series³. The variation in compound forma-

¹ With Calvert J. A. C. S. 33, 1924 (1911); Martin, *ibid*, 36, 1589 (1914); Coleman, *ibid*, 38, 271 (1916); Mullinix, *ibid*, 41, 72 (1919); Reed, 41, 1921 (1919).

² Kendall and Booge, *loc. cit.*, p. 2324 (1917). Gross, *loc. cit.*, pg. 7.

³ The order of increasing conductivity is given as that of increasing electrolytic solution tension, Schlesinger and Coleman, *loc. cit.*, p. 278.

tion should parallel the change in conductivity. To test the validity of these conclusions, a representative series of the formates was examined, namely, K, Na, Li, NH_4 , Ba, Ca, $\text{Mg} \cdot \text{Zn}$, Ni, Pb, Cu and Ag. The solubilities of these formates were determined, using the freezing-point method, as described below.

Due to unavoidable complications, inherent in the nature of the solvent (i. e. of X), it was not possible to work with silver. In order that the increase of compound formation as R is varied below H might be demonstrated, several members of the acetate-acetic acid series were studied. Na, Zn, Ni, Fe (ic) and Ag were taken as representing the different portions of the electromotive series.

The agreement between the deductions from the theoretical considerations discussed, and the results of these experiments ought to furnish sufficient evidence to demonstrate the applicability of the generalization given above to systems of the type $\text{HX}-\text{RX}$.

EXPERIMENTAL

EXPERIMENTAL PROCEDURE

Freezing-point curves for mixtures of formate and formic acid were determined in the usual manner¹. Points on the curves were taken at intervals of from 2 to 3 molecular %; at points of change of phase, the intervals were small enough to fix accurately the different branches of the curve. Each point was determined at least twice.

Those mixtures which gave a melting-point² below sixty degrees (60°C) were investigated in freezing point tubes by

¹ See Kendall and Booge, J. A. C. S. 38, 1718 (1916), and Landon, loc. cit., for discussion of method. In some cases, i. e., at low temperatures, considerable supercooling was encountered. The mixtures were then cooled in CO_2 -acetone paste and allowed to warm up slowly, with stirring, to induce crystallization.

² The temperatures which follow refer to the point at which a negligibly small amount of the solid phase is in equilibrium with the solution.

the usual method. Every precaution was exercised to insure, as far as possible, anhydrous conditions. The addition of formate to the acid was done with the aid of a specially designed weighing bottle¹, thus reducing exposure to a minimum. The stirrer was connected to the stopper by means of rubber tubing, the system being in this way entirely closed. The composition given for any of these solutions is accurate within less than $\pm 0.05\%$. Above about 60°C , recourse was had to sealed bulbs², because of the increasing vapor pressure of the formic acid. These bulbs were so blown as to reduce the air space to a minimum, thus decreasing the amount of solvent present as vapor to a negligible magnitude. The composition given for solutions whose freezing-points were measured in bulbs, may be taken as accurate within ± 0.1 molecular per cent.

The bath in which the tube or bulb was placed during the determination of the melting point, varied with the temperature range in which the point lay. Those baths used, and the temperature interval of their use, were:

Acetone + CO_2 (solid)	-	-	-	Up to -25°C .
HNO_3 + ice	-	-	-	-25° — 0°
NaCl + ice	-	-	-	-15° — 0°
Water	-	-	-	0° — 100° .
70 mol. % H_2SO_4 ; 30 mol. % $(\text{NH}_4)_2\text{SO}_4$				above 100° .

Considerable attention was paid to the factors affecting thermal equilibrium between the tube or bulb and the bath. This resulted in the following precautions being observed, to avoid any appreciable error from this cause:

1. The tube and bath were stirred constantly.

¹ See Landon, Columbia University Dissertation (1920), pg. 9, for detailed description and cut of this bottle.

² Points in bulbs were, of course, determined under excess pressure, i. e., the vapor pressure of the system plus the pressure of the enclosed air. Since the limiting temperature was 160°C , and the effect of pressure on the freezing points so very small (probably $< 0.01^{\circ}$ per atmosphere), there would be no advantage in attempting, if it were possible, to reduce all freezing-points to atmospheric pressure.

2. The temperature was changed slowly enough so as to maintain¹, as nearly as practicable, thermal equilibrium throughout the heating process.

3. The bulbs were sufficiently thin to prevent lag when the above precautions were observed².

The effects of draughts, and radiation at higher temperatures, were excluded by the use of an asbestos shield surrounding the bath. This shield had glass windows to permit observation of the bath.

TEMPERATURE MEASUREMENT

Temperatures were measured by means of three mercury thermometers, graduated in tenths of a degree (C.), and having the respective ranges, $-35^{\circ} - +25^{\circ}$; $0^{\circ} - 100^{\circ}$; $100^{\circ} - 200^{\circ}$. These were calibrated at 0° and 100° , and the two with lower range were compared with a certified thermometer at intermediate points. The $100^{\circ} - 200^{\circ}$ thermometer was tested at the boiling points of pure monobrombenzene and aniline (Kahlbaum), giving results in agreement with the literature. Hence it was considered as correct within the limits of experimental error (as discussed below).

The correction for exposed stem was determined experimentally³ by measuring constant temperatures⁴ with the thermometer exposed, and then repeating with the thread entirely immersed. The length of thread exposed was the same as would be left outside the bath in a determination of a melting point. The corrections obtained were plotted against tempera-

¹ App. 0.2° per minute was the average rate of heating. This was varied slightly, according as the slope of the curve changed. Where the rate of change of composition with temperature was high, the rate of heating was diminished. The rate was increased slightly under the reverse circumstances.

² This is proven by concordant results when points on the same portion of a curve were determined by either method.

³ The apparatus used for this determination consisted of a glass tube, resembling the outer jacket of a Victor Meyer apparatus, to the top of which a Liebig condenser was attached. Its use was suggested by Dr. P. M. Gross.

⁴ Boiling liquids of good quality, not necessarily ultra pure, give temperatures constant to 0.1° for a sufficient length of time to permit both measurements being taken.

tures, and from the graph so made, the stem correction for any intermediate point could be read¹.

Precision of Measurements—The freezing-point of a mixture prepared by the above method and determined with one of the thermometers just described, possesses a definite precision value. This depends not only upon the temperature interval in which the point lies, but also upon the nature of the curve. This is due to the fact that it is easier to determine, with any desired precision, a point which lies on a flat curve than one which is on a steep curve².

The fact that both of these factors, temperature and slope, have to be considered makes it difficult to give any definite probable values. Those which follow are to be taken as approximations, true for the average type of curve only³:

Temperature Interval	Possible Error
—35° to —10° - - -	± 0.2° to ± 0.5°
—10° to + 100° - - -	± 0.1° to ± 0.2°
100° to 200° - - -	± 0.2° to ± 0.5°

ANALYSIS OF COMPOUNDS

The composition of the solid phase separating, in every case where it was not evident from the curve, was determined by analysis. A mixture of suitable composition was prepared, and the substances to be analyzed frozen out. The compound was then collected in a Gooch crucible, the solution being drawn through by suction. The filtration was carried out under anhydrous conditions⁴. The solvent adhering to the crystals was removed by sucking air dried by CaCl_2 through for sufficient time to guarantee complete removal.

¹ While it is evident that these corrections hold exactly only when the temperature surrounding the stem is the same as when the corrections were determined, a change of .3° or 4° in room temperature produces no appreciable effect upon the values.

² Flat and steep refer to the slopes of the curves—the change of temperature with respect to a slight change in composition is small and large on the respective curves.

³ As Boogés, Kendall and Booge, loc. cit. To be exact, distinction must be made between points determined in bulbs, and in open tubes.

⁴ Water decomposed the compounds. The apparatus was so set up that when it was necessary to maintain a low temperature during filtration, the funnel could be surrounded by a freezing mixture.

The composition was calculated from the volume of standard alkali required to neutralize a weighed amount of the compound. Check determinations were run to preclude the possibility of unremoved acid giving erroneous and misleading results.

FORMATE SYSTEMS

Formic Acid.

The formic acid used was prepared from Baker and Adamson c. p. acid by treatment with boron trioxide to remove the water it contained. The mixture was distilled in vacuum, moisture being excluded¹. The acid which was used froze between 8.35°—8.5°, and was generally better than 8.4°².

SYSTEM FORMIC ACID—POTASSIUM FORMATE

This system was investigated partially, by Groschuff³, who determined the solubility of potassium formate in formic acid between 0° and 100°C. He used a method similar to that employed in this work, and succeeded in isolating an acid salt $\text{KCHO}_2 \cdot \text{H}_2\text{CO}_2$, which, according to the investigator, underwent transition before it melted. In view of the incompleteness of the work, it was thought advisable to repeat the part already done, in addition to completing that part left undone. As will be seen from the data, the course adopted was justified. Groschuff's work was not only incomplete, but was erroneous as well.

The potassium salt was prepared by dissolving a pure sample of potassium carbonate in 90% formic acid. After expelling the CO_2 , the hydrate of potassium formate⁴ was crystallized from the solution. This salt was dehydrated and dried as completely as possible by prolonged heating just below the

¹ Berichte 14, 1709 (1881). See particularly, Schlesinger and Martin, loc. cit., whose apparatus and procedure were followed.

² Varying values are given in the literature, 8.5° being probably correct. 8.43°, Peterson, Ber. 13, 1191 (1880). 8.5° Walden, Trans. Far. Soc. 6, 71 (1910). 8.52°, Novak (by extrapolation), Phil. Mag. (5) 44, 828. 8.6°, Schlesinger and Calvert, loc. cit.

³ Berichte 36, 1783 (1903).

⁴ Groschuff, loc. cit., who also discusses the hygroscopicity of the salt, which is very great.

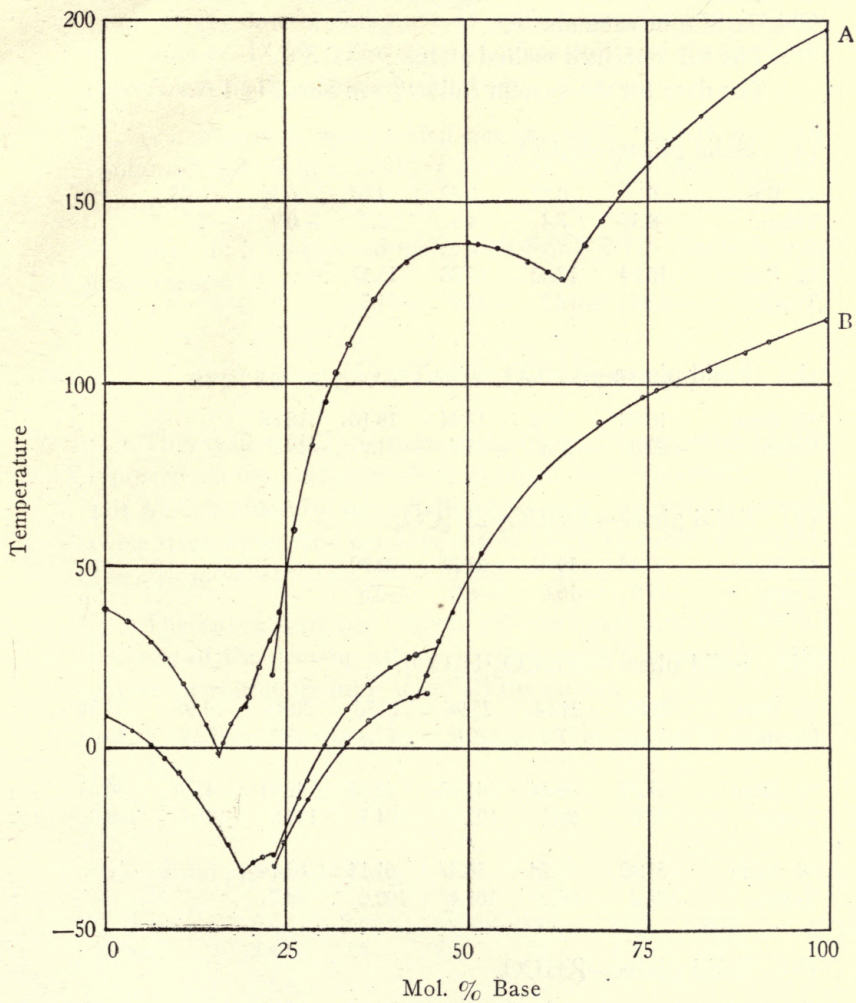


Fig. I.

(A)—Potassium Formate—Formic Acid. (subtract 30° from the temperature readings).

(B)—Ammonium Formate—Formic Acid.

melting point. The last trace of water was removed by recrystallization from absolute ethyl alcohol, and dessication over 99% H_2SO_4 in vacuum.

The salt obtained melted at $167.5^\circ \pm 0.5^\circ\text{C}.$ ¹

The data for the system follow; see also Fig I A.

(a) Solid phase— H_2CO_2 .

% Base	0	0.97	3.02	4.73	6.36	8.43
Temp.	8.35	7.4	4.9	2.2	-0.9	-5.7

% Base	10.74	12.63	13.88	15.57
Temp.	-12.6	-18.7	-23.8	-31.5

(b) Solid phase— $\text{KHCO}_2 \cdot 3\text{H}_2\text{CO}_2$ (?)

% Base	16.32	16.52	17.44	18.10	18.88
Temp.	-29.0	-27.3	-23.5	-21.7	-19.5

(c) Solid phase— $\text{KHCO}_2 \cdot 2\text{H}_2\text{CO}_2$.

% Base	19.48	19.91	21.21	22.79
Temp.	-19.0	-16.0	-8.0	-0.6

(d) Solid phase— $\text{KHCO}_2 \cdot \text{H}_2\text{CO}_2$.

% Base	23.04	24.14	25.98	28.56	30.41	31.97	33.74
Temp.	-10.1	7.3	29.9	53.0	65.1	72.9	80.6

% Base	37.29	38.34	41.68	42.63	42.91	45.95	50.25
Temp.	93.0	96.1	103.2	104.3	104.6	107.5	108.6

% Base	51.49	54.24	58.47	61.14	63.14
Temp.	108.2	107.2	103.4	100.6	98.7

(e) Solid phase— KHCO_2

% Base	66.45	68.71	71.24	75.18	77.75	82.41	86.68
Temp.	108.1	114.5	122.3	130.7	135.8	143.6	150.0

% Base	91.24	100.00
Temp.	157.3	167.5

¹ The salt used by Groschuff melted at $157^\circ\text{C}.$

Analyses:

(b) It was not practicable to carry out this analysis, because of the low temperature at which compound undergoes transition (-17.5°). The slope of curve indicates the probable correctness of the composition given.

(c) Analysis was carried out at -4°C . 0.3838 gm. salt contained 0.2050 gm. acid. Calculates to 67.9 mol. % acid. Theoretical 2:1 is 66.7%.

(d) 1:1 compound melts at $-108.6^{\circ} \pm 0.1^{\circ}$. Analysis was unnecessary.

SYSTEM SODIUM FORMATE—FORMIC ACID

This system had also been partially, and as the work herein reported shows, erroneously examined by Groschuff¹. The salt was obtained by recrystallizing a pure commercial sample twice from water, and dehydrating at 140°C to constant weight. The salt gave a melting point of $255^{\circ} \pm 1^{\circ}$.²

The curve does not extend beyond approximately 160°C , because of the decomposition of the acid at this point³. This places an automatic limit upon all the curves.

The data for the system follow. The curve is given in Fig. II A.

(a) Solid phase— H_2CO_2 .

% Base	0.0	1.04	2.92	4.61	6.35	8.72
Temp.	8.4	7.5	5.3	3.0	0.4	-3.8

% Base	10.50	12.58
Temp.	-7.6	-12.8

¹ Loc. cit.

² Groschuff obtained 253° as the m. pt. of sodium formate.

³ Richter, Org. Chem. 1,266—Lorin, Jahresbericht uber Fortschritte Chemie, 28, 515 (1876).

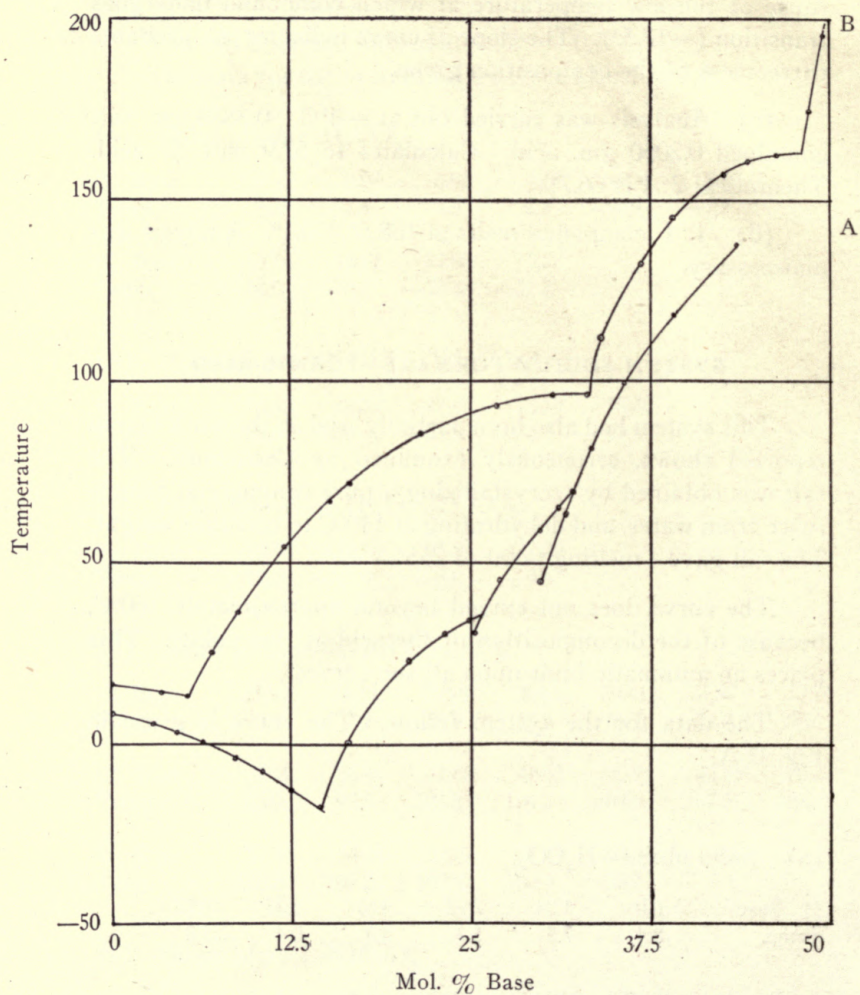


Fig. II.

(A)—Sodium Formate—Formic Acid.

(B)—Sodium Acetate—Acetic Acid.

(b) Solid phase— $\text{NaHCO}_2 \cdot 2\text{H}_2\text{CO}_2$.

% Base	14.52	16.45	18.18	20.69	21.13	21.86	23.23
Temp.	-17.4	0.3	10.7	22.9	24.4	26.3	30.5

% Base	24.43	24.91
Temp.	33.1	34.5

(c) Solid phase— $\text{NaHCO}_2 \cdot \text{H}_2\text{CO}_2$.

% Base	25.18	25.90	27.00	27.10	28.39	29.80	31.15
Temp.	31.0	37.3	45.2	45.6	52.2	59.0	65.1

% Base	31.65	32.14
Temp.	67.5	69.6

(d) Solid phase— NaHCO_2 .

% Base	29.80	31.65	33.40	35.71	39.10	42.79	43.47
Temp.	45.1	63.6	81.2	99.3	118.6	135.2	137.7

Analyses:

(b) 0.2842 gm. compound contained 0.1615 gm. acid; equivalent to 0.1674 mole acid to 0.0888 mole salt or 66.06 mol. % acid. Theoretical 2:1 is 66.7%.

(c) 0.2013 gm. compound contained 0.0814 gm. acid; equivalent to 0.1770 mole acid to 0.1763 mole salt; or 50.1 mol. % acid. Theoretical 1:1 is 50.0%.

SYSTEM LITHIUM FORMATE—FORMIC ACID

Groschuff¹ also worked with this system, but did not do the part of the curve of chief theoretical interest. His work was extended to complete the curve as far as possible.

Lithium formate was prepared from a pure sample of the carbonate and 90% B. and A. acid. The hydrate was crystallized from the solution, dehydrated at 100°C², and the dry salt

¹ Groschuff, loc. cit.

² It decomposes to water and anhydrous salt at 94°C—Groschuff, loc. cit.

recrystallized from alcohol, and dessicated over 99% H_2SO_4 in vacuum.

The data for the system are given below :

(a) Solid phase— H_2CO_2 .

% Base	0.0	1.58	3.47	5.33	7.09	8.93	10.75
Temp.	8.4	7.0	5.2	3.2	+1.1	—1.3	—3.5

% Base	12.23	13.99	18.19	19.56	21.15	22.24	23.49
Temp.	—5.6	—8.2	—14.6	—17.1	—19.8	—21.7	—23.5

% Base	24.33
Temp.	—25.0

(b) Solid phase— LiHCO_2 .

% Base	23.49	23.93	25.31	25.91	26.38	27.71
Temp.	18.0	34.0	80.0	90.5	97.9	113.1

% Base	29.87	31.98	33.04	35.01	36.13
Temp.	131.2	145.1	150.4	159.1	163.5

Analysis proved (b) to be the neutral salt.

SYSTEM AMMONIUM FORMATE—FORMIC ACID

The existence of an acid salt of ammonium (equimolecular) was shown by Groschuff¹, after Reik² had failed to find one. No complete examination of the system has been previously undertaken.

The ammonium salt was prepared by passing ammonia into 90% acid. The acid was cooled in ice until it was almost saturated; it was then allowed to warm up sufficiently to insure the separation of the neutral salt. This salt was collected on

¹ Groschuff, *Berichte*, 36, 4351 (1903).

² Reik, *Monatshefte*, 23, 1033 (1902).

a Büchner funnel, and recrystallized from absolute alcohol; it was desiccated over 99% H_2SO_4 in vacuum. The salt gave a melting point of $117.3^\circ \pm 0.2^\circ$, that reported by Groschuff being 116° .

The data for the system are given below and in Fig. I B:

(a) Solid phase— H_2CO_2 .

% Base	0.0	1.53	3.70	6.28	8.19	10.14	12.43
Temp.	8.47	7.0	4.5	0.6	-2.8	-6.9	-12.6
% Base	14.86	17.11	18.95				
Temp.	-19.8	-26.9	-33.8				

(b) Solid phase— $\text{NH}_4\text{HCO}_2 \cdot 3\text{H}_2\text{CO}_2$ (?).

% Base	20.43	21.73	23.33
Temp.	-31.3	-30.0	-29.3

(c) Solid phase— $\text{NH}_2\text{HCO}_2 \cdot \text{H}_2\text{CO}_2$, two crystalline modifications, less soluble (stable)—needles; more soluble (unstable)—prisms.

% Base	23.33	24.83	25.41	26.64	27.90		
Temp.*	-32.5	-26.0	-23.5	-18.7	-14.0		
Temp.†	—	—	—	-13.7	-8.7		
% Base	30.11	33.25	36.29	39.30	41.90	42.94	44.38
Temp.*	—	1.3	7.4	11.3	13.8	14.3	15.0
Temp.†	+0.7	10.4	17.3	22.2	24.9	25.8	—

(d) Solid phase— NH_4HCO_2 .¹

% Base	44.38	46.06	47.87	51.88	59.98	68.23	74.32
Temp.	20.4	29.3	37.5	53.1	74.3	89.5	96.5
% Base	76.20	83.46	88.41	91.64	100.00		
Temp.	98.5	103.7	108.5	111.7	117.3		

* Unstable.

† Stable.

¹ At the higher points, upon keeping the solutions in molten condition for a while, there appeared to be a tendency for the melting points to be slightly lowered, making it difficult to check points. This must be due to decomposition in the liquid state, possibly to formamide, although this generally takes place at a much higher temperature— 180° - 230° Beilstein 1,395.

Analyses:

(b) could not be analyzed. Nature of curve makes it probable that composition given is correct.

(c) The two crystalline modifications have the same composition, 0.5846 gms. compound gave 0.2432 gm. acid—equivalent to 0.5285 to 0.5413 moles or 49.4 molecular % acid (Theory 1 : 1 is 50%).

SYSTEM BARIUM FORMATE—FORMIC ACID

There has been no work on solubilities in this system reported in the literature. The barium salt was prepared from the carbonate and acid. It was recrystallized from water three times, and dried at 140°C.

The data are given below :

(a) Solid phase— H_2CO_2 .

% Base	0.00	0.91	1.74	2.30	3.73	4.67	5.12	6.95
Temp.	8.4	7.2	6.1	5.1	2.6	+0.5	-0.3	-4.9

(b) Solid phase— $\text{Ba}(\text{HCO}_2)_2 \cdot \text{H}_2\text{CO}_2$.

% Base	8.52	8.86	9.23	9.83	10.03	10.75
Temp.	9.5	15.5	19.0	24.9	26.5	31.8

Analysis:

(b) 0.4262 gm. cpd. contained 0.0733 gm. acid; equivalent to 0.1593 to 0.1552 moles acid and salt respectively. This calculates to 50.66 mol. % acid. Theory, 1 : 1 is 50%.

SYSTEM CALCIUM FORMATE—FORMIC ACID

No previous work in this system could be located in the literature.

The calcium salt was prepared by a method analogous to that used for barium formate.

The data are given below :

(a) Solid phase— H_2CO_2 .

% Base	0.00	0.16	0.48	0.71	0.93	1.27	1.53
Temp.	8.4	8.1	7.7	7.4	7.2	6.9	6.6

(b) Solid phase— $\text{Ca}(\text{HCO}_2)_2$.

% Base	0.39	0.57	0.83	1.10	1.26	1.35	1.54	1.61
Temp.	128.6	100.0	79.0	61.0	49.7	45.5	35.0	30.0

Analysis proved (b) to be the neutral salt.

It is seen from the data that calcium formate in formic acid exhibits retrograde solubility. This is not surprising, since the same phenomenon occurs in aqueous solutions of many calcium salts¹.

SYSTEM MAGNESIUM FORMATE—FORMIC ACID

This system has not been previously investigated. The salt was prepared by dissolving the oxide (Kahlbaum) in acid, and dehydrating the crystallized salt (a dihydrate) at 110°C . The resulting salt was slightly basic, but not sufficiently so to have any effect upon the results obtained².

It was not possible to obtain a curve giving the solubility of this salt. It was found that those mixtures which yielded clear solutions would not crystallize to any solid phase other than formic acid. Furthermore, on heating other mixtures, to get a more concentrated solution, there occurred separation of solid, which dissolved very slowly on cooling. Measurements showed that the magnesium salt was soluble up to a concentration of 0.2 molecular per cent. at room temperature (about 25°C).

SYSTEM LEAD FORMATE—FORMIC ACID

No work on this system has been reported in the literature. The salt was prepared by double decomposition from lead ni-

¹ Washburn, Physical Chemistry, pg. 354. Lumsden, J. Chem. Soc. (London), 81, 355 (1902).

² Analysis showed a basicity of much less than 1%. Since the salt was only very slightly soluble, the amount of base (or of water produced) is of a negligible magnitude.

trate and sodium formate. The resulting precipitate was thoroughly washed and recrystallized twice from water. It was dried at 140°C. All of the points, the data for which are given below, were determined in bulbs, due to the relatively insoluble nature of the salt.

Solid phase— $\text{Pb}(\text{HCO}_2)_2$.

% Base	0.21	0.30	0.42	0.51
Temp.	20.0	73.1	109.4	124.5

SYSTEM ZINC FORMATE—FORMIC ACID

No previous work in this system has been reported. The salt was prepared by the method used for the Ba and Ca salts. The solubility was less than 0.1 mol. % at 140°C.

SYSTEM COPPER FORMATE—FORMIC ACID

No previous work has been reported. The salt was made from a pure sample of basic carbonate and acid. The hydrate was crystallized from water and dehydrated, at about 80°C, giving the bright blue neutral salt¹. The solubility was less than 0.1% at 135°C.

SYSTEM NICKEL FORMATE—FORMIC ACID

No work on this system has been reported in the literature. The salt was prepared from the carbonate and c. p. acid. The hydrate, which was crystallized from water, was dehydrated at 140°C. It was soluble to less than 0.1 molecular % at 140°C.

SILVER FORMATE

Inasmuch as it was desired to show the variation in compound formation below hydrogen in the electromotive series, attempts were made to investigate the silver system. The salt is described in the literature² as a white crystalline salt, decomposed by boiling water to give Ag and CO_2 . The descrip-

¹ Voss, Liebig's Annalen 266, 33 (1891).

² Beilstein, 1, 395. Richter, Organische Chemie, 1, 266.

tion is not strictly accurate. It was found impossible to keep the salt in the presence of water for the length of time necessary to filter the solution by suction. The decomposition is not due to light, as has also been suggested¹, but undoubtedly is caused by the aldehydic nature of the acid itself.

The salt was isolated by precipitating it in absolute methyl alcohol. It is not, however, sufficiently stable to work with; it decomposed in a dessicator over H_2SO_4 , even though protected from the light.

ACETATE SYSTEMS

Acetic Acid: 100% acetic acid was prepared from glacial acetic acid, by using the method of Gross². From the freezing-point of the acid, and DeVisser's³ figures, the percentage of water was calculated, and the amount of acetic anhydride required to react with that amount added to the acid. The mixture was refluxed for about 30 hours and then distilled.

The acid used froze between 16.5° and 16.6° .⁴

SYSTEM SODIUM ACETATE—ACETIC ACID

This system has not been previously examined with respect to solubility. The literature mentions the existence of the acid salts $\text{NaAc} \cdot 2\text{HAc}$ melting at 80° and the equimolecular compound melting "above 140°C ".⁵ The "cryohydrate" of this system has been studied⁶, i. e., the location of the eutectic and the composition of the solid phase on either side were determined.

The salt used was a pure Baker and Adamson hydrate, which was recrystallized from water, and maintained at 140° for over a week. The resulting salt gave no evidence of even a trace of water.

¹ Richter, loc. cit.

² Dissertation, Col. University, 1919, pg. 15.

³ DeVisser, Rec. Trav. Chim. Belg., 12, 101 (1893).

⁴ DeVisser, loc. cit., obtained 16.67° hydrogen scale, equivalent to 16.60° mercury scale.

⁵ See table I.

⁶ Vasiliev, J. Russ. Phys. Chem. Soc., 41, 753-7 (1909).

The data for the system are given below and in Fig. II B:

(a) Solid phase— $\text{H}_4\text{C}_2\text{O}_2$.

% Base	0.0	0.83	3.59	5.40
Temp.	16.5	16.1	14.3	13.1

(b) Solid phase— $\text{NaH}_3\text{C}_2\text{O}_2 \cdot 2\text{H}_4\text{C}_2\text{O}_2$.

% Base	7.11	8.92	12.17	15.27	16.58	21.55	26.86
Temp.	25.3	36.7	54.3	66.9	71.9	85.7	93.2

% Base	30.72	33.03	33.16
Temp.	9.61	96.25	96.3

(c) Solid phase— $\text{NaH}_3\text{C}_2\text{O}_2 \cdot \text{H}_4\text{C}_2\text{O}_2$.

% Base	34.03	36.87	39.06	42.54	44.25	46.28
Temp.	112.0	132.3	145.2	157.0	160.6	162.3

(d) Solid phase— $\text{NaH}_3\text{C}_2\text{O}_2$.

% Base	48.76	49.49
Temp.	174.4	195.5

SYSTEM ZINC ACETATE—ACETIC ACID

No previous work in this system has been located in the literature. Zinc acetate (Kahlbaum) was dehydrated at 100°C . The anhydrous salt was only very slightly soluble in acetic acid—being soluble to 0.1 mol. % at 130°C .

SYSTEM FERRIC ACETATE—ACETIC ACID

Neutral, anhydrous ferric acetate cannot be prepared. The salt used was basic, probably as slightly so as it is possible to obtain it. It was prepared¹ by treating a solution of ferric acetate in about 90% acetic acid, with an excess of acetic anhydride, and refluxing the mixture. The resulting crystals were dried with ether. The value obtained in this experiment is

¹ The salt was part of a sample made by Professor J. E. Zanetti, of Columbia, to whom the author wishes to express his thanks.

the maximum solubility that ferric acetate could have, since the neutral salt would probably be less soluble than the basic salt used.

The salt was soluble to less than 0.07% at 140°C.

SYSTEM NICKEL ACETATE—ACETIC ACID

There has been no work on this system reported in the literature. The salt was prepared by dissolving the carbonate in c. p. acid, and crystallizing the hydrated acetate from the solution. This compound was dehydrated and treated with acetic anhydride to prevent the formation of any basic salt.

The salt was soluble to 0.44% at 140°C.

SYSTEM SILVER ACETATE—ACETIC ACID

No previous work has been reported. Silver acetate was prepared from silver nitrate and sodium acetate. The precipitate was thoroughly washed, and recrystallized from water. It was dried over 99% H_2SO_4 in vacuum. The measurements could not be carried very high (not above 115°), as the acetate underwent reduction at higher temperature. The silver salt is not very soluble in acetic acid. The data are given below:

% Base	0.094	0.204
Temp.	76.0	115.0

CONDUCTIVITY MEASUREMENTS

To complete the series of conductivities compiled by Schlesinger and his collaborators¹, measurements were made of the conductivity of systems Ba, Pb, and Mg formates in formic acid. The measurements were made in a cell of the Freas type, with platinized electrodes. Inasmuch as the precision required for a qualitative comparison of conductivities was not very high, it was not found necessary to balance out the capacity of the cell by means of a condenser. The results are accurate to better than $\pm 1\%$.

¹ Loc. cit.

Conductivities were determined in a thermostat maintained at $25.00^{\circ} \pm 0.01^{\circ}$. A Leeds and Northrup bridge of the Kohlrausch type, with telephone receiver tuned to 1000 cycles was used. The current was supplied by a constant speed high frequency generator (1000 cycles/sec.).

No attempt was made to get formic acid of conductivity as low as that obtained by Schlesinger and his co-workers¹. That used in this work had a specific conductivity of $7.3-7.5 \times 10^{-5}$ reciprocal ohms.

CONDUCTIVITIES

Base	Conc. ²	$S \times 10^4$	$Sa \times 10^4$
Barium	0.2758	11.92	11.85
	0.1869	8.551	8.478
	0.0923	4.902	4.827
	0.0474	2.649	2.575
Lead	0.1047	2.462	2.387
	0.0477	1.370	1.295
Magnesium	0.0919	3.006	2.931
	0.0479	1.758	1.683

DISCUSSION OF RESULTS

An examination of the experimental results will disclose the extent of agreement between them and the corresponding consequences of the hypothesis proposed in the beginning of the paper.

(a) Compounds Isolated.

The curves in general, and the particular compounds isolated may be first compared. The addition compounds crystallized, generally, as needles, whereas the neutral salts give in most cases crystals belonging to the rhombic system. Table II gives the compounds actually isolated, with the freezing-point relationships of each.

¹ S. and Martin, J. A. C. S., 36, 1590 (1914).

² Conc. in equivalents per liter.

³ S=Specific conductivity of solution in reciprocal ohms.

⁴ Sa=S—Specific conductivity of solvent.

TABLE II.

Compound	Transition Temp.	Composition solution in equilibrium at trans. temp. (mol. %)
$\text{KHCO}_2 \cdot 3\text{H}_2\text{CO}_2$ ¹	—18.0	19.6
$\text{KHCO}_2 \cdot 2\text{H}_2\text{CO}_2$ ¹	4.0	23.9
$\text{KHCO}_2 \cdot \text{H}_2\text{CO}_2$	Melts at 108.6°	
$\text{NH}_4\text{HCO}_2 \cdot 3\text{H}_2\text{CO}_2$ ¹	—29.0	23.3
$\text{NH}_4\text{HCO}_2 \cdot \text{H}_2\text{CO}_2$ ²	prisms 27.0	45.6
	needles 14.8	43.1
$\text{NaHCO}_2 \cdot 2\text{H}_2\text{CO}_2$ ¹	35.6	25.7
$\text{NaHCO}_2 \cdot \text{H}_2\text{CO}_2$	70.5	32.3
$\text{Ba}(\text{HCO}_2)_2 \cdot \text{H}_2\text{CO}_2$ ¹	undeterminable ³	

The order of increasing complexity, as well as of increasing stability of the complexes, is seen to be that required by the hypothesis. Potassium forms the most complex compounds, and of the eight different compounds isolated, the equimolecular potassium acid formate is the only one sufficiently stable to give an actual melting point⁴. The form of the curve (Fig. I A) in the neighborhood of the maximum indicates some dissociation of the compound into its components⁵. The more complex components undergo transition before they melt.

Next in order of complexity and stability to the potassium compounds, are those of ammonium formate (Fig. I B). A comparison of the extent of compound formation⁶ shows sodium and ammonium formates to be solvated (in solution) to practically the same extent. The increased complexity and stability in the case of the ammonium compounds, is undoubtedly due to the temperature factor⁷—the lower temperature at which the ammonium complexes exist, decreases their tendency

¹ Compounds not previously mentioned in the literature.

² Two modifications not previously noted.

³ See below.

⁴ Groschuff, loc. cit., did not obtain a melting-point, as noted above.

⁵ The relation between stability of the compound and the sharpness of the maximum is discussed by Kendall and Booge, loc. cit., pg. 1728; also by Kremann, Monatshefte 25, 1215 (1904).

⁶ See section (b), following.

⁷ See particularly, Gross, loc. cit., p. 29.

to decompose. It is interesting that the equimolecular compound exists in two crystalline forms, the stable form being the only one previously mentioned¹.

The sodium compounds are quite unstable, undergoing transition into compounds of a lower order of complexity long before their respective melting points are reached.

The same is true of the barium compound, the transition point of which is given as indeterminable. The last few points on the curve are probably metastable. On standing, crystals separate which are probably the anacid salt. Not enough of these could be obtained for an analysis, nor could they be made to separate in fine enough form to enable one to determine a melting-point, i. e., to locate the stable curve. Solutions more concentrated than the last one could not be obtained at 140°C.

Lithium formate, though soluble in formic acid, does not form any isolable complex with it. It is noteworthy that this base, that of the least electropositive of the alkali metals, yields no compound, whereas barium, the most electropositive of the common alkaline earths, forms an equimolecular compound with formic acid. Other properties also place these two metals in this order².

(b) Extent of compound formation from the relative slopes of the curves.

It has already been emphasized that addition compounds may be formed in solution, and yet not be sufficiently stable to allow of their being isolated³. By applying a more general method of detecting compound formation, it was shown that a better estimate of relative degrees of solvation in solution was obtainable. This method consists in the determination of the extent of deviation of the curve representing the data collected, from the ideal curve⁴, the equation of which is

¹ Groschuff, loc. cit., who gives the transition temperature as 23.5°, instead of 27.0° obtained in this work.

² Abegg, *Hand. Anorg. Chem.* 2-1, 117. Soddy, *Chemistry of the Radio Elements*, p. 44, gives the order of the elements on the basis of their physical properties as K, Na, Ba, Sr, Li, Ca.

³ Kendall, *J. A. C. S.*, 36, 1731 (1914). Kendall and Booge, loc. cit., p. 1730, Kendall, Booge and Andrews, loc. cit., 2309.

⁴ Washburn, *Phys. Chem.* p. 174, Kendall and Booge, *ibid.*

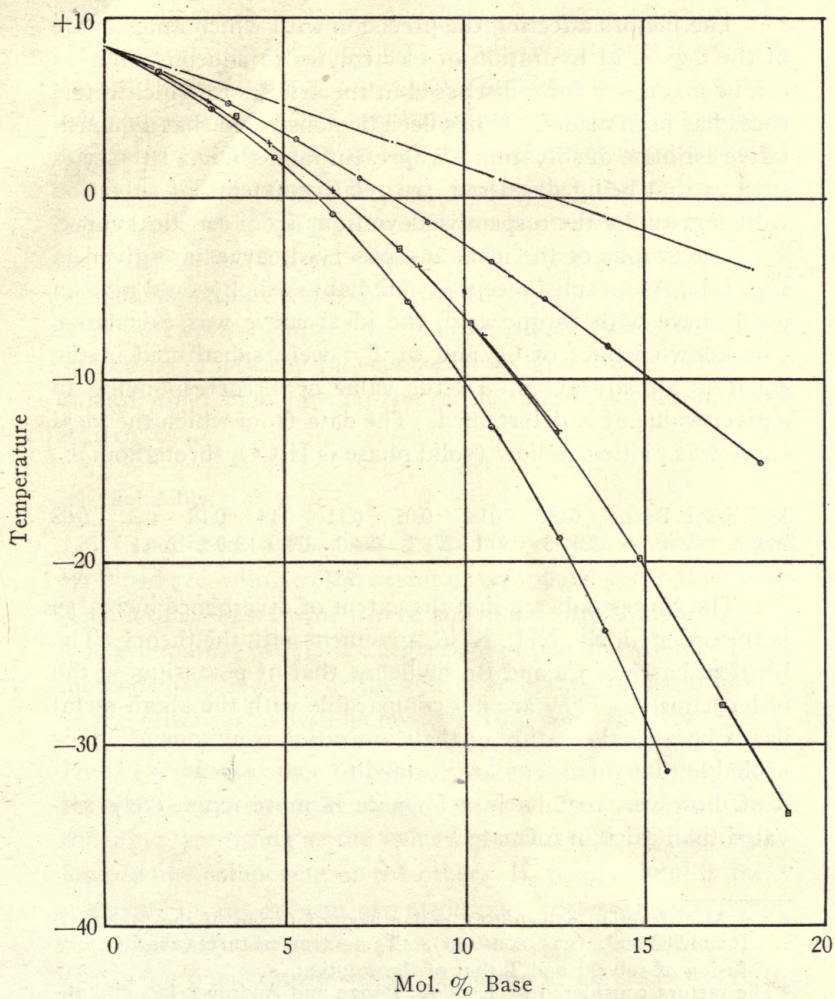


Fig. III.

Freezing-point depressions. In order of increasing depression:
a—Ideal b—Lithium c—Sodium d—Ammonium e—Potassium.

$$-\log_e X = \frac{Q}{RT_0} \left(\frac{T_0}{T} - 1 \right)^1$$

The factors affecting the precision with which an estimate of the degree of hydration of electrolytes in aqueous solution can be made, are fully discussed in the articles to which references has been made². It has been demonstrated that a quantitative estimate of solvation is at present impossible. In a series such as that being discussed, the relative extents of solvation will be given by the respective deviations from the ideal curve.

The graphs of the ideal and observed curves are given in Fig. III. As no substance was obtainable which would give an ideal curve with formic acid, the ideal curve was calculated. The known values of Q^3 and of T_0^4 were substituted in the equation already given, and the value of T corresponding to a given value of X determined. The data from which the ideal curve was plotted, follow (solid phase is H_2CO_2 throughout):

Mol. fract. Base	0.00	0.02	0.05	0.11	0.14	0.18	0.22	0.08
Temp.	281.43	280.1	278.1	274.0	271.9	269.1	266.1	276.1

The curves indicate that the extent of divergence increases in the order Li, Na, NH_4 , K, in agreement with the theory. The bivalent bases of Ca and Ba lie below that of potassium in the order named⁵. They are not comparable with the alkali metal bases, because the nature of their ionization is unknown⁶. It is probable that three ions are formed to some extent. It is evident, however, that barium formate is more extensively solvated than calcium formate.

¹ X = Mol. fraction solvent; Q , molar heat of fusion of the "solvent." $R = 1.988$ cal. (gas constant). T_0 is temperature (absolute) of fusion of solvent and T that of the solution.

² The factors considered by Kendall, Booge and Andrews, loc. cit., obtain in the system under consideration, and the conclusions arrived at in that paper are equally significant here.

³ $Q = 2421.2$, Berthelot, C. R. 78, 716 (1874).

⁴ $T_0 = 281.43$ Peterssen, Ber. 13, 1191 (1880).

⁵ Ca and Ba are not given in Fig. III, at 1.5% the f. pt. is 6.6° ; Ba at 1.5% is at 6.3° .

⁶ Schlesinger and Mullinix, loc. cit., pg. 75. Schlesinger and Bunting, J. A. C. S. 41, 1945 (1919).

The divergence which has been noted results essentially from ionization and from solvation. Ionization increases the number of moles of solute and hence produces abnormal depressions of the freezing-point. Solvation removes solvent, thereby increasing the molecular fraction $(1-X)$ of solute, and consequently has a similar effect. It is not possible to determine exactly what part of the total effect is produced by each of these factors. In view of the fact that it has been definitely established that "ionization is preceded by combination between solvent and solute, and is indeed a consequence of such combination"¹, such an attempt appears to be superfluous. It is noteworthy, however, that the alkali bases, which are ionized to practically the same extent², give curves which are quite distinct showing that the second factor, solvation, is operative.

(c) Solubility.

In addition to those bases which have been considered and classified according to the extent of compound formation, there remain those bases which were not sufficiently soluble to allow a determination of relative degrees of solvation by either of the methods described. For these it is necessary to use solubility as the criterion, as will be evident from what follows.

In an ideal binary system, the equation given above³ represents the equation of the solubility curve of either substance in the other, according as the values substituted for Q and T_0 belong to one component or the other. If, then, solubility measurements in any solvent are made on a series of salts having approximately the same values of Q and T_0 , the solubility at any given temperature will be the same in all cases where the solutions resulting are ideal.

¹ Kendall and Booge, loc. cit., p. 2324.

² Schlesinger et al, loc. cit.

³ See, particularly, Washburn and Read, Proc. Nat. Acad. Sci. 1, 191 (1915). C. A., 9, 1520 (1915). Washburn, Principles of Physical Chemistry, pg. 172.

If, however, there occurs combination between the solvent and some of the substances, the curves for these will fall away from the maximum more rapidly than the ideal¹. The substances will be, at any given temperature, more soluble than those which give ideal solutions.

In actual practice, a series of salts in which the values of Q and T_0 are the same throughout, is never encountered. This fact removes the possibility of obtaining any quantitatively comparable data. In the case of the series under consideration, the values of T_0 ² are several hundred degrees above room temperature. Because of the large value of T_0 , the solubility will of necessity be very small in all systems in which no compound formation occurs. The order of solubility will accordingly correspond qualitatively with the extent to which combination between the two components of the system takes place.

The greater the extent of compound formation, the greater the solubility ought to be (provided the comparison be made of analogous compounds at the same temperature). Since it has been postulated that compound formation should vary with the position of the metal in the electromotive series, it follows that a similar variation in solubility should occur.

Examination of the data (also Figures I and II) shows that the solubility, at 25° say, does decrease to a minimum from potassium through the alkaline earths to zinc and copper. Ammonium formate is far more soluble than potassium formate, but this is undoubtedly due to the low value of T_0 (300° absolute for the equimolecular compound). The only real exception is in the case of the lead salt, which is too soluble. While no explanation can be offered at present, it is significant that in sulfuric acid³, and in water, the corresponding lead salts are also out of their proper place.

¹ This is evident from Fig. III.

² The values of T_0 are not determinable, except in the cases of Na, NH_4 and K. The melting-points of K and NH_4 are low (see above). The temperatures of decomposition are generally above 300°C. See *Berichte*, 51, 399 (1918).

³ Unpublished work for Davidson, who discusses the subject of solubility in greater detail.

It has already been mentioned that it was not possible to demonstrate with formates alone that the solubility of the bases passed through a minimum and then, with increasing divergence between H and the metal (whose position is below hydrogen), increases again. The supplementary experiments with the acetates are more satisfactory in this respect.

Sodium acetate (Fig. II B) is very soluble in acetic acid; its solubility is of the same order of magnitude as that of sodium formate in formic acid. Two compounds were isolated. The compound $\text{NaH}_3\text{C}_2\text{O}_2 \cdot 2\text{H}_4\text{C}_2\text{O}_2$ undergoes transition at its melting point, $96.3^\circ \pm 0.1^\circ$ (the literature gives $80^\circ\text{C}.$)¹. The equimolecular compound undergoes transition at 163° , before reaching its melting point. The curve resembles very much that for sodium sulfate in sulfuric acid².

Zinc acetate is soluble to only a slight extent, 0.1% at 130°C , and the results obtained with a slightly basic ferric acetate indicate a still smaller solubility in the case of the neutral ferric salt. Silver acetate is several times as soluble as the acetates of these metals. The acetate of nickel is abnormally soluble, 0.44% at 140° , for which fact no immediate explanation is available.

The experimental results taken collectively indicate that compound formation and the related properties, decrease to a minimum and then increase again, when the metal (R) in the system $\text{HX} \cdot \text{RX}$ is varied from the upper to the lower end of the electromotive series.

While the increase in compound formation below hydrogen in the acetate series is not as large as might be expected (for example, it is very striking in the sulfate series), it is doubly significant, because it brings up for consideration a point which might otherwise be overlooked. On comparing the data available in the different series— RSO_4 in H_2SO_4 , RHCO_2 in H_2CO_2 , etc., it becomes evident that while the alkali bases are soluble to practically the same extent in each series, the rate at which the solubility falls off as R is varied through the alkaline earths toward hydrogen, is different in the several series.

¹ Lescoeurs, loc. cit.

² Landon, loc. cit., pg. 23.

Thus, the solubility of the sulfates falls off less rapidly than that of the formates, the order being $\text{RSO}_4 < \text{RHCO}_2 < \text{RH}_3\text{C}_2\text{O}_2 < \text{ROH}^1$. There is an inverse variation in the extent to which the solubility increases in the case of the bases of the more noble metals. Here the sulfates show the most pronounced increase in solubility, and the increase in the acetate and hydroxide series is small. The complete significance of these facts and their proper explanation may be evident after several series of fairly strong acids have been examined, and the influence of X completely determined.

(d) Discussion of Conductivity Measurements.

TABLE III.

Base	Cpds. Isolated	Conc. ²	Λ ³	Conc. ²	Λ ³
NH_4	1:3; 1:1	*0.04646	67.93	*0.09293	65.74
K	1:3; 1:2; 1:1	*0.05480	65.74	*0.09464	63.37
Na	1:2; 1:1	*0.04381	62.19	†0.0923	60.01
Li	none	*0.9574	58.79	*0.0902	56.68
Ba	1:1	0.0474	54.32	0.0923	52.30
Sr	not examined	*0.0476	53.57	†0.0923	49.34
Ca	none	†0.0474	51.37	†0.0923	46.66
Mg	none	0.0479	35.14	0.0919	31.90
Pb	none	0.0477	27.15	0.1047	22.74

From this table it is evident that the variation of compound formation with the position of the metal in the electromotive

¹ To test this statement, a few measurements on calcium acetate in acetic acid were made. At 30°, calcium acetate is soluble to less than 0.35%; calcium formate is soluble to 1.6%; calcium sulfate (or rather, a 1:3 compound) to 5.4%, and calcium hydroxide (at 20°) to 0.04%, each in the corresponding solvent. Calcium formate, it has been noted, shows retrograde solubility, and therefore the difference in solubility between it and calcium acetate would be less at higher temperatures.

² Conc. in equivalents per liter.

³ Λ is equivalent conductivity in reciprocal ohms.

* Schlesinger and collaborators' results, loc. cit.

† Results marked thus †, are calculated by interpolation from the rate of change of Λ with the concentration in the neighborhood of this value of the concentration. It does not change the order of the bases, although necessarily inexact. Also, the difference in concentration in the different cases to be compared, is too small to affect the order of the bases.

series is paralleled by the change in conductivity. The agreement between the freezing-point measurements and conductivity measurements is good.

It is again difficult to fix exactly the correct positions of lithium and barium. Lithium has a higher equivalent conductance than barium, although the latter gives a stable compound with formic acid while lithium does not. The light lithium ion may be more mobile than the barium ion.

The exact position of ammonium formate among the bases is not easily located. Although less extensively solvated than potassium, it shows greater conductivity. This is probably explained by the fact that the ammonium complexes are formed are less stable¹, and therefore undergo dissociation into ions to a greater extent than do the analogous potassium complexes.

Lead, in the conductivity results also, takes the same abnormal position as before. Its solubility was slightly lower than that of magnesium, and the conductivity results agree with this fact.

The results indicate that the high conductivity of formates in formic acid noted by Schlesinger and his collaborators, is due, as predicted by the generalization, to extensive combination between solvent and solute. The extent of combination decreases in order from potassium through the alkali metals and alkaline earths to lead, and is paralleled practically exactly by the diminution of conductivity.

The agreement of the experimental results with the argument advanced at the beginning of the paper, affords considerable support to the general validity of the propositions there stated.

SUMMARY:

The attempt has been made to extend the generalization correlating compound formation and chemical diversity to a series of non-aqueous systems of the type $HX \cdot RX$. On the basis of the generalization, the extent of compound formation,

¹ Gross (dissertation, pg. 7), has shown that the extent of ionization depends upon: (1) The extent of the compound formation— $AB + CD \rightleftharpoons AB \cdot CD$ and (b) The extent of dissociation of the complexes into ions of opposite charge $AB \cdot CD \rightleftharpoons (AB \cdot C)^+ + D^-$.

and hence of ionization, should vary with the difference in character of the two components.

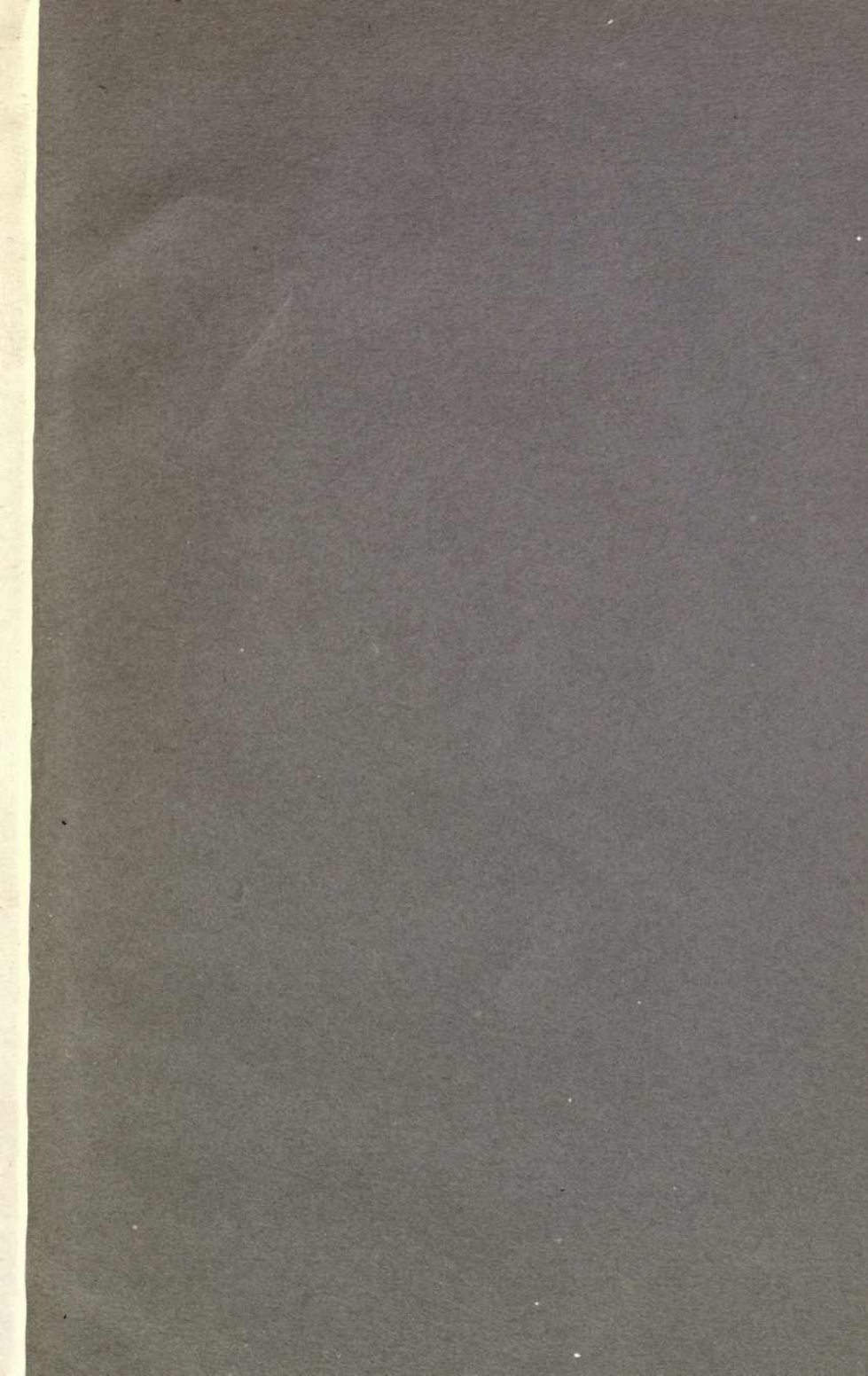
The use of the relative positions of the metals and hydrogen in the electromotive series as the criterion of diversity has been proposed. From this it follows that as R is varied from one extreme of the series to the other, the extent of compound formation should diminish to a minimum (near hydrogen) and then increase again.

This conclusion has been tested experimentally by the determination of freezing-point curves of representative formate-formic acid and acetate-acetic acid systems. In addition, conductivity measurements have been employed to test the validity of the argument advanced.

The results have agreed strikingly with the deductions from the fundamental assumptions. Five new acid formates were isolated. In the formate series, the extent of combination between the two components decreases to a minimum as the position of R is varied from potassium through the series toward hydrogen. The acetate series exhibits a similar variation, with a slight increase in the extent of combination in the case of the silver system. The change in conductivity and in solubility parallel the variation in extent of combination. This experimental evidence indicates the probable validity of the assumptions to which reference has been made.

VITA.

Howard Adler was born in New York City on January 9, 1896, and attended the grade and high schools of that city. He received the degree of B. S. from the College of the City of New York in February, 1916. From 1916 to 1917 he taught in the Department of Chemistry of the College of the City of New York, at the same time attending the graduate school of Columbia University. In June, 1917, he received from Columbia the degree of M. A. From September, 1917, until February, 1919, he was in the United States Army. In February, 1919, he resumed graduate work at Columbia University.



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